

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP012395

TITLE: A Review of Recent Experiments and Calculations Relevant to the Kinetics of the HF Laser

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Gas and Chemical Lasers and Intense Beam Applications III Held in San Jose, CA, USA on 22-24 January 2002

To order the complete compilation report, use: ADA403173

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP012376 thru ADP012405

UNCLASSIFIED

# A review of recent experiments and calculations relevant to the kinetics of the HF laser

Gerald C. Manke II\* and Gordon D. Hager  
Air Force Research Laboratory  
Directed Energy Directorate  
Kirtland AFB, NM 87117

## ABSTRACT

An abbreviated review of rate coefficients relevant to HF laser kinetics modeling is presented. The literature has been surveyed from the last published review in 1983 to the present. Updated HF Einstein emission coefficients are tabulated. This brief summary of a more detailed review addresses rate coefficients relevant to HF generation, reactive quenching, self-relaxation, and vibrational relaxation by a selection of atoms and molecules. In addition, a review of recent experiments and theoretical calculations relevant to the role of rotational non-equilibrium in HF lasers is presented. A list of recommended temperature dependent expressions for critical reaction rate coefficients is given.

## 1. INTRODUCTION

Since its invention in the mid-1960's, the HF laser system has been extensively studied and developed to the point where megawatt-class devices can be built. In fact, most of the research in the recent past has focused on large-scale laser technology demonstrations. Despite the enormous effort expended to accomplish this, a complete understanding of all facets of HF laser performance is still evolving and is not complete. For example, research continues into the role of reagent mixing and heat transfer between the fluids and the construction material of the device. Combustor instabilities and other complex, transient, fluid dynamical features also impede our understanding of the laser's performance.

The only way to achieve insight into the details of the HF laser is to employ computational fluid dynamical (CFD) codes that can integrate the complex fluid properties with the myriad chemical reactions that occur in the laser cavity. Unfortunately (although perhaps not surprisingly considering the complexity of the problem), CFD codes have had limited success at accurately modeling real HF laser systems. As a result, both the laser performance data and the reaction rate constants used to baseline the models have come under increased scrutiny in recent years. This scrutiny has uncovered serious questions about the kinetics package that have yet to be answered conclusively. These questions include the importance of rotational nonequilibrium, the magnitude of various quenching processes, the role of three body and heterogeneous fluorine atom recombination, and other fundamental properties such as Einstein coefficients.

The main topics of this report (in order of their presentation) are Einstein coefficients and relevant kinetic measurements. It is not within the scope of this document to discuss fluid dynamics issues, such as recently developed 3 dimensional computational fluid dynamics (CFD) codes or new algorithms to model mixing or optical resonators.

## 2. EXPERIMENTS AND CALCULATIONS RELEVANT TO HF LASER MODELING

### 2.1 Einstein Coefficients

The Einstein coefficients used by most HF CFD codes are based on the values found in the Handbook of Chemical Lasers<sup>1</sup> (which are in turn, based on the empirical calculations of Herbelin and Emanuel<sup>2</sup>), and have not been updated in over 25 years. Table 1 gives a representative sample of the Handbook's HF vibration-rotational Einstein emission coefficients as well as the more recent (and preferred) results of Setser and co-workers<sup>3</sup>, see below. While the agreement is generally good for the first 3 vibrational levels, large differences are apparent as the vibrational quantum number increases. In 1991, Zemke<sup>4</sup> and co-workers published a potential surface based on the spectroscopically determined potential of Coxon and Hajigeorgiou<sup>5</sup>, adjusted to reproduce the proper long-range behavior by including both dispersion and exchange effects<sup>6</sup>. In the same publication, Zemke and co-workers provided an *ab initio* dipole moment function that spanned the same range of internuclear distances as the complete potential energy curve. The resulting Einstein coefficients should be the most reliable theoretical values. Shortly after the publication of Zemke's results, Setser and co-workers produced an extensive set of vibration-rotational Einstein A coefficients for HF/DF and HCl/DCI<sup>3</sup>. Their calculations used an RKR potential and the *ab initio* dipole moment function of Ogilvie<sup>7</sup>. Their results are in excellent agreement with Zemke.

Considering the importance of the Einstein A coefficients in calculating the stimulated emission cross section and the gain, the most accurate values available should be employed. Unfortunately, Zemke and co-workers calculations were only for a limited number of rotational quantum numbers. We recommend that the HF CFD codes be updated with the results of Arunan, Setser, and Ogilvie<sup>3</sup>.

## 2.2 HF Kinetics

Most modern day HF CFD codes have kinetics packages that are based on a 1976 Aerospace Corporation technical report by N. Cohen & J. Bott<sup>8</sup>. This report and its 1977 supplement<sup>9</sup> contained a thorough review of contemporary literature results up to 1977 and recommendations for rate constants related to the HF laser. An update was published 5 years later in 1982<sup>10</sup>, and a few relevant reactions were reviewed again in 1983 by Cohen & Westberg<sup>11</sup>. Beyond these reports, there have only been a handful of critical evaluations of kinetic data relevant to the HF laser. A 1982 review article by Leone summarizes hydrogen halide vibrational energy transfer and contains rate coefficients relevant to the HF laser system<sup>12</sup>. In 1983, George Hart of the Naval Research Laboratory reviewed the pulsed DF chemical laser codes and the corresponding kinetic database<sup>13</sup>. Although his report was specifically for DF, it contains a wide variety of relevant and helpful evaluations for the HF laser. The following paragraphs summarize the most recent and reliable calculations and experiments relevant to HF generation and quenching.

### 2.2.1 HF Generation - $H + F_2$ and $F + H_2$

The generation of HF(v) in the HF laser can proceed via one of two reactions,  $H + F_2$  or  $F + H_2$ , which have significantly different product vibrational distributions. The reaction of atomic hydrogen with molecular fluorine (often referred to as the "hot" HF generation reaction) produces highly vibrationally excited HF, while  $F + H_2$  (the "cold" HF generation reaction) produces only moderate vibrational excitation, see below. The vibrational distribution for  $H + F_2$  peaks at  $v = 6$  and extends up to  $v = 9$ . Table 3 summarizes the vibrational distributions recommended by the Cohen and Bott<sup>8-11</sup> reviews as well as the measured distributions from a variety of experiments. Most experimental measurements, particularly those of Polanyi<sup>14</sup>, Jonathan<sup>15</sup>, and Tardy<sup>16</sup> analyzed their data using Einstein coefficients that have since been shown to be inaccurate<sup>2, 17, 18</sup>. Hence, corrected distributions using the recommended set of A coefficients<sup>3</sup> are shown in parentheses in Table 3.

In general, the available experimental results are in reasonable agreement for the HF(v) distribution. The only uncertainty concerns the nascent population of  $v \geq 8$ . On the low end, the fast flow reactor studies of Setser<sup>19</sup> and Kaufman<sup>20</sup> found no  $P_8 - P_{10}$ , while on the high end the pressure-pulse chemiluminescence mapping experiments of Tardy<sup>16</sup> found substantial populations for  $v = 8 - 9$ . The presence of at least some  $P_8 - P_{10}$  is supported by the infrared chemiluminescence studies of Polanyi and Jonathan, who reported minor  $P_8 - P_{10}$ . The nascent vibrational populations from recent theoretical calculations<sup>21</sup> are in satisfactory agreement with experiment but have slightly narrower distributions with small but nonzero population of  $v = 8 - 10$ .

Surprisingly, the Cohen and Bott reviews recommend no initial population of  $v = 0 - 2$ , even though all of the experimental measurements (most of which were available at the time) indicate small, but nonzero  $P_1$  and  $P_2$ . Clearly, some initial population of  $v = 1 - 2$  is indicated by the experimental evidence, and in light of this, we recommend the distribution given in the final column of Table 2. This distribution attempts to encompass the general observation that  $v = 8 - 9$  is present but at lower populations than suggested by Tardy. The recommended values for  $v = 1 - 6$  are simply the average and one standard deviation from the 5 experimental measurements. Recommendations for  $v = 0$ ,  $v = 7 - 10$  are estimates based on the experimental values and have significantly larger error bars ( $\pm 50\%$  or more). Our distribution is similar in shape to the DF(v) distribution generated by the  $D + F_2$  reaction<sup>16, 22</sup>, which falls off rapidly beyond the peak at  $v = 9 - 10$ .

The total rate constant for  $H + F_2$  has not been firmly established. The 1982 Cohen & Bott review<sup>10</sup> gives  $k(T) = 5.0 \times 10^{-15} T^{1.5} \exp(-845/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the 1983 Cohen & Westberg recommendation<sup>11</sup> is essentially the same,  $4.8 \times 10^{-15} T^{1.4} \exp(-667/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ . In both cases, the recommended value was based on the experiments of Homann and co-workers<sup>23</sup> and unpublished transition state theory calculations of Westberg and Cohen<sup>24</sup>. The 1981 Baulch kinetic<sup>25</sup> database recommends  $k = 1.46 \times 10^{-10} \exp(-1210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $T = 290 - 570 \text{ K}$  and points out that Homann's result is significantly smaller (approximately a factor of 2 at 300 K) than previous results by Rabideau<sup>26</sup>, Vasil'ev<sup>27</sup>, and Goldberg<sup>28</sup>. A new measurement of the total H atom removal rate constant and the nascent HF distribution was performed recently by Heaven and co-workers<sup>29</sup>. They report  $k = 2.4 \pm 0.4 (2\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The  $F + H_2$  reaction is a prototypical system for fundamental reaction dynamics, and as such, has been a favorite subject for both theoretical and experimental state-to-state reactive scattering studies. The reaction is particularly amenable to molecular beam studies and vibrationally state resolved differential cross sections have been measured<sup>30-36</sup>.

Corresponding high level *ab initio* calculations and simulations<sup>37, 38</sup> have achieved very good agreement with experiment. The vibrational distribution remains unchanged from the 1982 Cohen & Bott report<sup>10</sup>, 0.00 : 0.15 : 0.55 : 0.30 for  $v = 0 - 3$ .

A recent review by Persky & Kornweitz<sup>39</sup> has refined the overall rate constant for the  $F + H_2$  reaction. Following a detailed examination of relevant publications they recommend  $k(T) = 1.1 \pm 0.1 \times 10^{-10} \exp(-(450 \pm 50)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the 190 - 376 K temperature range, and  $2.43 \pm 0.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. This compares reasonably well with literature reviews published in 1983<sup>11</sup> ( $k(T) = 4.5 \times 10^{-12} T^{0.5} \exp(-319/T)$  and  $k_{298} = 2.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), 1992<sup>40</sup>, and 1997<sup>41</sup> ( $k(T) = 1.4 \times 10^{-10} \exp(-(500 \pm 200)/T)$  and  $k_{298} = 2.6 \pm 0.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), as well as the Cohen & Bott reviews of 1977<sup>9</sup> ( $k(T) = 2.7 \times 10^{-10} \exp(-805/T)$  and  $k_{298} = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and 1982<sup>10</sup> ( $k(T) = 4.32 \times 10^{-12} T^{0.5} \exp(-307/T)$  and  $k_{298} = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The most recent review by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry<sup>42</sup> adopted the Persky recommendation<sup>39</sup>. Unfortunately, the limited temperature range of the Persky expression is problematic for HF laser modeling, since the laser typically operates at substantially higher temperatures. To date, there has been only one experiment that has measured  $k(F + H_2)$  above 376 K. Heidner and co-workers<sup>43</sup> monitored the time-resolved infrared emission of product HF following multi-photon dissociation of  $SF_6$  in the presence of  $H_2$  over the 295 - 765 K temperature range. The resulting Arrhenius expression for  $k(F + H_2)$  is  $2.2 \pm 0.4 \times 10^{-10} \exp(-(595 \pm 50)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , just 7 % smaller than Persky's at room temperature but 40% larger if Persky's expression is extrapolated to 765 K. Persky & Kornweitz<sup>39</sup> considered Heidner's results "problematic with regard to the calculated kinetic isotope effect." Indeed, the Heidner experiment gave a temperature independent kinetic isotope effect while the accepted value is

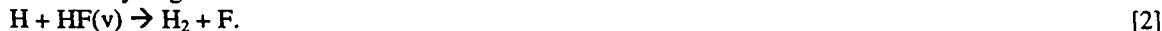
$$\frac{k_{F+H_2}}{k_{F+D_2}} = 1.04 \pm 0.02 \exp((186 \pm 5)/T). \quad [1]$$

In lieu of more data for  $T > 376$ , we recommend the conclusions of Persky and Kornweitz<sup>39</sup> for the 190 - 376 K temperature range and the expression of Heidner and co-workers<sup>43</sup> for  $T > 376$  K.

Some CFD codes<sup>44</sup> include F atom reactions with vibrationally excited  $H_2$  even though this process was not included in the original Cohen and Bott compilations. There have been no specific experimental measurements to support or refute this assumption and we do not recommend inclusion of reactive processes that involve vibrationally hot  $H_2$ . In any case, it is unlikely that inclusion of these reactions will have any effect on the overall performance of the laser because  $[H_2(v > 0)]$  should be extremely small.

### 2.2.2 Reactive Quenching

Vibrationally excited HF can be removed by hydrogen atoms by V-R,T inelastic collisions or by chemical reaction to give molecular hydrogen and an F atom:



In principle, microreversibility enables one to calculate the rate constant for [2] from the extensive data available for the well-studied  $F + H_2$  reaction. In fact, numerous theoretical studies have attempted to do this using the  $F + H_2$  potential energy surface<sup>45-49</sup>. According to these calculations the barrier to F atom transfer is large,  $\sim 33 \text{ kcal mol}^{-1}$ , and reaction [2] should be slow for  $v < 3$ <sup>50-52</sup>. This is consistent with the experimental results of Heidner and co-workers<sup>53-55</sup> who measured  $HF(v)$  deactivation by H atoms directly using HF laser induced fluorescence, and the flow tube measurements of Kwok & Wilkins<sup>56</sup>. These experiments report a large change in the  $HF(v)$  removal rate constant for  $v = 1-2$  vs. 3. This change is generally attributed to the opening of the reactive channel for  $v \geq 3$ . However, according to Heidner<sup>54, 55</sup> only a fraction of the total  $H + HF(3)$  encounters that result in removal of  $HF(3)$  proceed via chemical reaction and the upper limit for reactive quenching,  $k(H + HF(3) \rightarrow H_2 + F)$ , is  $5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The 1981 Baulch kinetics database<sup>25</sup> makes no recommendation for  $k_2$  because the experimental evidence available at the time was inconsistent with the data for the well established forward reaction,  $F + H_2$ . While there have been no new experiments (for thermal collisions) since the work of Heidner and Bott<sup>53-55</sup>, the available theoretical calculations support their slower reaction rate constants<sup>8, 57</sup>.

### 2.2.3 HF Self-Relaxation

One of the most active areas of HF kinetics research in the past 15 years has been in the study of HF self-relaxation and vibrational energy transfer. The importance of these processes is acute because this is the dominant relaxation pathway in the HF laser. Unfortunately, a consensus regarding the magnitude of the rate constants had not been reached prior to 1982. For example, the 1977 Cohen and Bott<sup>9</sup> compilation contains moderate to large rate constants for single- and multi-quantum V-R,T deactivation of HF by ground state HF



while the 1982 Cohen and Bott package<sup>10</sup> includes only single quantum deactivations. Significant differences also exist for the HF V-V energy transfer reactions such as



Implicitly included in reaction [3] are the V-R redistribution processes that produce highly rotationally excited HF:



As will be discussed in detail below, this quenching process is of special interest because it has the potential to contribute significantly to rotational nonequilibrium.

Shortly after the publication of the 1982 review<sup>10</sup>, the Crim group at the University of Wisconsin<sup>58-62</sup> and the Kaufman group at the University of Pittsburgh<sup>20, 63-66</sup> undertook a major effort to characterize the total self-relaxation rate constants and the mechanism for HF self-relaxation. Crim's group used a double resonance type of experiment where the vibrationally excited HF molecules were prepared in discrete ro-vibrational states by a pulsed laser. The time resolved fluorescence and/or  $\Delta v = 1$  absorption signals were analyzed to determine total quenching rates and relaxation mechanisms. Kaufman, on the other hand, prepared vibrationally excited HF in a flow reactor where dilute flows of H or F atoms (generated by a microwave discharge) were reacted with a variety of F or H atom donors. The IR emission was collected with an InSb detector and circularly variable filter. A modified Stern-Volmer analysis was applied to the quenching data. Table 3 compares the experimentally determined rate constants for HF self-relaxation with a variety of other experiments<sup>67-78</sup>, relevant calculations<sup>79-83</sup>, and the standard kinetics packages<sup>8-11</sup>. The agreement for  $v = 1 - 7$  is, in general, excellent and  $k_3$  is well established. The experimental relaxation rates scale as  $v^{2.9}$  and are independent of the initial rotational quantum number.

In addition to total quenching rate constants, the Crim and Kaufman laboratories also determined the relaxation mechanism. Kaufman's group argued strongly for a V-T,R mechanism (rather than V-V energy transfer) based on Lambert-Salter plots<sup>20, 63-66</sup> and the magnitude of the rate constants. In particular, they pointed out that if the predominant mechanism were V-V energy transfer, (eg.  $\text{HF}(7) + \text{HF}(0) \rightarrow \text{HF}(6) + \text{HF}(1)$ ) then the rate constant for the exothermic reverse process would be 100 times greater than the gas kinetic limit. Crim's double resonance experiments were able to quantify the role of V-V energy transfer. They found that the fraction of inelastic  $\text{HF}(v) + \text{HF}(0)$  room temperature encounters that proceed via V-T,R relaxation, is 1.0,  $0.41 \pm 0.10$ ,  $0.56 \pm 0.05$ ,  $0.84 \pm 0.05$ , and  $0.98 \pm 0.19$  for  $v = 1 - 5$ , respectively<sup>59, 60, 62</sup>. For  $v > 3$ , vibrational energy transfer to the ground state collision partner plays a relatively minor role in the relaxation process. Both Crim and Kaufman agree that multi-quantum relaxation is unimportant<sup>62, 63</sup> even though work by Pimentel and Thompson (see below) suggested the possibility of multi-quantum V-R transfer with  $\Delta v$  as large as 5. Crim probed the role of multi-quantum deactivations directly and found that  $0.98 \pm 0.19$  and  $0.87 \pm 0.21$  of the relaxed  $\text{HF}(4)$  and  $\text{HF}(5)$  molecules, respectively, appear in the next lower vibrational level<sup>62</sup>. It is important to note that Crim and co-workers' results are based on the assumption that V-T,R processes that produce metastable high rotational states (which would not be detected in their experiment) can be neglected. The invariance of the vibrational relaxation rate constant with initial rotational quantum number and the work of Leone (see below) tend to validate this assumption.

Finally, Crim and co-workers found that the rate constants for HF self-relaxation are inversely dependent on temperature<sup>59, 61</sup>. Crim and co-workers interpret their temperature dependent data in terms of relaxation probabilities. The functional form of the fitting function suggests that long-range forces dominate the relaxation process:

$$P_v(T) = AT^{-m} \quad [6]$$

where  $P_v = k_v/k_c$  ( $k_c$  is the gas kinetic rate constant for a collision diameter of 0.25 nm) and  $A$  and  $m$  are fitting parameters. Strangely, the  $A$  values determined by our fits (where  $m = 1.3$  was fixed) vary significantly from Crim's analysis<sup>61</sup>:  $A(\text{Crim}) = 22, 370, 880$ , and  $1850$  for  $v = 1, 3, 4$ , and  $5$  respectively, while  $A(\text{this work}) = 12, 315, 764$ , and  $1610$  for the same  $v$  levels. Nonetheless, considering the overall agreement in the literature for  $v = 1 - 7$  and the accuracy of double resonance technique, we recommend Crim's HF self-quenching rate constants<sup>61</sup>. The temperature dependence of  $v \geq 6$  has not been measured. If the temperature dependence found for  $v = 1 - 5$  (i.e.  $k_v = P_v * k_c = k_c * A * T^{-1.3}$ ) is applied, then  $A(6) = 3107$  and  $A(7) = 4339$  are calculated from the measured room temperature values<sup>20</sup>.

#### 2.2.4 HF Relaxation and V-V Energy Transfer with $\text{H}_2$

There have been several studies of  $\text{HF}(v)$  relaxation by a variety of molecular quenchers. Table 4 summarizes the results for  $\text{Q} = \text{H}_2$ , which are the most relevant to HF laser kinetics<sup>20, 71, 75, 84-87</sup>. With the exception of the work by Poole and Smith<sup>75</sup>, the agreement for the total quenching rate constants is good for  $v = 3 - 5$ . The mechanism for the quenching is generally believed to be V-T,R for  $v = 3 - 5$  for two important reasons. First, V-V energy transfer from  $\text{HF}(v)$  to  $\text{H}_2$  is endothermic for all single vibrational quantum changes in HF:



In fact, due to the anharmonicity of HF, the energy gap between HF( $\Delta v = -1$ ) and H<sub>2</sub>(0-1) increases with vibrational quantum number ( $\Delta E_{v,v} = -198 \text{ cm}^{-1}$  for HF(1) and  $-1171 \text{ cm}^{-1}$  for HF(7)). Secondly, if the endothermic V-V process were the dominant mechanism, then the exothermic reverse process



would be several times larger than the gas kinetic limit. Only for HF(1) does a V-V process seem possible, and indeed, vibrational energy transfer is the most likely mechanism for  $v = 1$ . For  $v > 1$ , however, the V-T,R process



should be the dominant mechanism.

The 1982 Cohen and Bott review<sup>10</sup> contains temperature and vibration dependent expressions for reactions [13] and [15] even though there is no convincing evidence for a temperature dependent quenching process<sup>85</sup>.

$$k_7(\text{ref. 11}) = 2.4 \times 10^{10} v^{0.35} T^{0.5} e^{(407 - \Delta E_v)/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad [10]$$

$$k_9(\text{ref. 11}) = v^{2.7} \left( 0.6 \times 10^{12} T^{-1} + 1.0 \times 10^4 T^{2.28} \right) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad [11]$$

For example, in 1973 Cohen & Bott measured the temperature dependence<sup>71</sup> ( $T = 295, 450 - 1000 \text{ K}$ ), of HF(1) deactivation by H<sub>2</sub> and found that the total deactivation ( $k_7 + k_9$ ) rate was independent of temperature (see Figure 4 of ref<sup>71</sup>). A year later Bott re-measured the temperature dependent quenching of HF(1) from 440 - 690 K and the data showed considerable scatter and only a weak temperature dependence<sup>84</sup>. Finally, in 1980 Bott and Heidner measured HF(1) and HF(3) quenching by H<sub>2</sub> at 295 and 200 K and found deactivation rate coefficients that were constant vs.  $T$  within their experimental error<sup>85</sup>. Clearly, there is not sufficient evidence to support a  $T$  dependent quenching rate constant.

Cohen & Bott's expression<sup>9</sup> for  $k_9$  significantly underestimates the measured values at room temperature, see Table 4. In fact, the 1982 package<sup>10</sup> eliminates the energy transfer reactions from H<sub>2</sub>(2) and H<sub>2</sub>(3) as well as the  $\Delta v > 1$  exchanges contained in the 1977 Cohen and Bott package because there is no specific experimental justification for them. We recommend the rate constant values listed in Table 4 for the V-T,R quenching of HF by H<sub>2</sub> and assign a  $T^0$  temperature dependence. The HF( $v$ ) + H<sub>2</sub>( $v'$ ) V-V energy transfer reactions (reaction [8]) are calculated from detailed balance.

### 2.3 Rotational Non-equilibrium

The question of rotational non-equilibrium for the HF laser system has been the subject of considerable controversy for many years<sup>88, 89</sup>. The presence of rotational non-equilibrium in the HF laser was first suggested by pulse initiated HF laser experiments by Pimentel and co-workers<sup>90-93</sup> which generated lasing on HF rotational transitions with  $J$  as high as 33 in the  $v = 1$  manifold and  $J = 29$  in the  $v = 0$  manifold. The observation of rotational laser emission is an extremely sensitive method for studying rotational occupancies because the population inversions needed to produce the laser emission are 100 times lower than for ro-vibrational transitions<sup>93</sup>. Pimentel's analysis of the transient behavior of the laser emission suggested that collisional V-T,R energy transfer reactions that populate the high rotational states were responsible for the observed positive gain, rather than direct pumping by the initiating reaction. A remarkably similar phenomenon was observed by Robinson and co-workers in their work with HF<sup>94</sup>, OH<sup>95</sup>, and NH<sup>96</sup>. Further experimental observations of emission from high  $J$  states following HF( $v$ ) quenching by CO, CO<sub>2</sub>, and HCN<sup>97, 98</sup> as well as quasiclassical trajectory calculations<sup>99, 100</sup> also support the assertion that high rotational states are produced in the V-T,R relaxation process.

The evidence is clear that the principal HF( $v$ ) relaxation mechanism in the HF laser environment is HF self-relaxation, and that the relaxation proceeds via V-T,R energy transfer. There are two important questions, however, that remain:

1) What are the specific products of the V-T,R process? Figure 1 summarizes the possible relaxation / energy transfer routes for HF( $v = 2$ ). The possible mechanisms include "true" V-T,R relaxation (the solid arrow) where the loss of a vibrational quantum results in some small amount of rotational and translational energy transfer to the HF( $v = 0$ ) quencher or near-resonant V-R redistribution (the broken arrows), where the quenched HF molecule relaxes to a lower vibrational state with a high rotational quantum number and very little energy is transferred to the quencher.

2) Are the high- $J$  HF molecules produced by the self-relaxation process "metastable"? In general, rotational relaxation rate constants ( $k \sim 10^{-10} - 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) are 10 - 100 times larger than vibrational deactivation rate constants ( $k \sim 10^{-12} - 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). However, because the separation between HF rotational levels is large, it is possible that  $k_{R,R,T} \approx k_{V,R,T}$  for sufficiently high  $J$  levels. If so, the vibrational relaxation process could significantly perturb the equilibrium rotational distribution and considerable errors could be realized when attempting to model real HF laser devices.

#### 2.3.1 Relevant Experimental Studies

As was discussed above, the self-relaxation measurements of Crim<sup>62</sup>, Kaufman<sup>63</sup>, and Moore<sup>77</sup> all concluded that multi-quantum deactivations were not important. In particular, Crim determined that  $0.98 \pm 0.19$  and  $0.87 \pm 0.21$  of the relaxed

HF(4) and HF(5) molecules, respectively, appear in the next lower vibrational level<sup>62</sup>. Kaufman came to the same conclusion and suggested that multiquantum relaxation processes account for less than 1% of the total measured relaxation rate constants<sup>63</sup>. Thus, any high-J states that are produced by the HF(v) self-relaxation process will almost certainly be found in the  $J = 0 - 20$  range of the next lower vibrational level.

The role of V-T,R relaxation reactions that populate high rotational states of the next lower vibrational level was addressed directly by the work of Haugen, Pence, and Leone<sup>101</sup> who measured the time dependent population of HF( $v = 0$ ,  $J = 10 - 14$ ) following pulsed generation of HF( $v = 1$ ,  $J = 6$ ). They concluded that a substantial fraction of the relaxation of  $v = 1$  occurs through the high lying rotational levels of  $v = 0$  (~20 - 40% of the total  $v = 1$  relaxation rate). The total phenomenological self-relaxation rate constant for HF( $v = 1$ ) (which by definition for  $v = 1$  is purely V-T,R) that they measured was identical to that determined in the double resonance experiments of Crim & co-workers<sup>58</sup>, ( $k = 1.46 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).

There has been a significant effort in the last 20 years to measure and predict rotational relaxation rate constants. Most recently, Muyskens, Copeland, and Crim<sup>102-106</sup> have measured rotational relaxation rate constants for HF( $v = 2 - 4$ ,  $J = 0 - 4$ ) with a variety of colliders. Their results generally confirm the standard view that rotational relaxation is 10 - 100 times faster than vibrational relaxation, particularly for the lower rotational quantum numbers ( $J = 0 - 8$ ). In addition to probing the role of V-T,R relaxation, the Leone group<sup>101</sup> has also measured rotational relaxation rate constants for  $v = 0$ ,  $J = 10 - 14$ . They found no experimental evidence of bottleneck effects and concluded that R-R,T rates always exceed the V-T,R rate by one or two orders of magnitude, even for  $J = 10 - 13$ . While their initial report<sup>101</sup> recommended R-R,T rate constants for  $v = 0$ ,  $J = 10 - 14$  which range from  $\sim 1.2 \times 10^{-10} - 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , subsequent measurements in the same laboratory suggested even larger values<sup>107, 108</sup>. The dominance of R-R,T relaxation over V-T,R and V-V energy transfer extends to other colliders besides HF. Taatjes and Leone, for example, measured the rotational relaxation rate constants for HF with a variety of collision partners (Ar, He, Ne, Kr, Xe,  $\text{H}_2$ , and  $\text{D}_2$ )<sup>107</sup> and found that while rotational relaxation by atomic species is very inefficient relative to HF,  $\text{H}_2$ , and  $\text{D}_2$  the rotational relaxation rate constants for atomic quenchers exceed the vibrational deactivation rate constants by several orders of magnitude:  $k(\text{R-R,T}) \geq 10^{-12}$  and  $k(\text{V-R,T}) = 10^{-17} - 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ . Leone and co-workers extended their measurements to non-ambient temperatures<sup>108</sup> and found that the HF V-T,R and R-R,T self relaxation reactions have a negative temperature dependence. The negative temperature dependence for rotational relaxation of HF( $v = 0$ ,  $J = 13$ ) is dramatic,  $T^{-1.57}$ .

In addition to the direct experimental measurements, there have also been attempts to extrapolate the low-J results to high-J using scaling laws and approximations such as the exponential energy gap law (EEG), the power law model (PLM), and the energy corrected sudden (ECS) approximation. Most of these efforts are summarized elsewhere<sup>88, 89</sup>, and while the accuracy of the models for predicting accurate R-R,T rates is the subject of some controversy, two general conclusions may be drawn from the relevant literature. 1) The PLM and ECS models give the most reliable results when compared to the existing high J and low J data. The EEG model consistently underestimates  $k(\text{R-R,T})$ , in some cases by several orders of magnitude. 2) The rate constants for rotational relaxation,  $k(\text{R-R,T})$ , are large,  $\geq 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ .

One noteworthy pair of reports<sup>109, 110</sup>, which claim to use a "more reliable form of the power scaling law" to calculate rotational energy transfer rate constants for  $v = 1 - 2$ ,  $J = 0 - 20$  give  $k(\text{R-R,T})$  values on the order of  $10^{-11} - 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , even for  $J = 20$ . On the other hand, their results suggest that rotational relaxation rates actually *increase* with vibrational energy, contrary to the results of Crim and coworkers<sup>102-106</sup>. The reliability of their model is, as the authors themselves admit, "an open discussion."

### 2.3.2 Relevant Theoretical Studies

No review of the role of rotational equilibrium for the HF laser would be complete without some discussion of quasiclassical trajectory calculation results, most notably those of Wilkins and Kwok<sup>79, 80, 111, 112</sup>, Thompson<sup>99, 100, 113, 114</sup>, and Billing<sup>83, 115-117</sup>. Billing's calculations found no evidence of high rotational state population, while the calculations by Wilkins and Thompson indicate that vibrational-rotational energy transfer is a relatively efficient process and that multiquantum deactivations occur on a fairly regular basis. In particular, Thompson<sup>99, 100</sup> calculated state-to-state collision cross sections for HF( $v = 4$ ,  $J = 20$ ) relaxation by He and reported 3.3, 6.7, 10.7, 18.5, and 38.24 a.u.<sup>2</sup> for  $\Delta v = 4, 3, 2, 1$  and 0, respectively. Calculations of this sort are usually very sensitive to the details of the potential surface on which the trajectories run, and unfortunately the requisite state-to-state cross sections required to evaluate the reliability of the theoretical calculations have yet to be measured. In general, the available experimental data does not support multiquantum deactivations.

In summary, the majority of the available evidence supports single vibrational quantum V-T,R relaxation which populates the high rotational states of the next lower vibrational state. There is no specific experimental evidence supporting multiquantum vibrational V-T,R relaxation. There is no doubt that near-resonant V-T,R relaxation plays an

important role in the HF chemical laser system and successful quantitative modeling depends on its inclusion. However, the available experimental evidence clearly shows that  $k(V-T,R) \ll k(R-R,T)$ , and in light of this, it is doubtful that high  $J$  states can act as "reservoirs" for near-resonant lasing levels. It seems more likely that the  $V-T,R$  process simply reduces the gain of the (1-0) and (2-1) transitions by reducing the population of the upper state while simultaneously increasing the population of the lower state.

### 3. CONCLUSIONS

Table 5 summarizes the recommendations of this report. Overall, many of the expressions found in the 1982 review by Cohen & Bott<sup>10</sup> remain valid today, in particular, the elimination of multi-quantum deactivation reactions that were a key feature of the 1977 kinetics package. These kinds of relaxation processes have been demonstrated to be very slow and can be safely neglected. Other areas of agreement include the total HF generation rate constants and the relaxation rate constants for collisions with molecular and atomic quenchers. A new measurement of the H atom removal rate constant for the "hot" reaction,  $H + F_2$ , would be particularly useful.

The major changes that we suggest occur in the Einstein coefficients, HF self-relaxation, and the nascent distribution for  $H + F_2$ . While in many cases these changes are minor, they may ultimately have significant effects to CFD calculation results due to enormous complexity of the HF laser system.

Clearly, there are some aspects of the HF kinetics package that should be re-examined experimentally. For example, in the case of  $HF(v) + F, H, Ar$ , and  $He$ , the recommended expressions are based on only a handful of measurements at a narrow range of temperatures. While the role of multi-quantum deactivations is very small according to the available experimental data, some believe<sup>44</sup> that the  $v^{2.9}$  scaling law for the HF self-relaxation process may be indicative of open multi-quantum deactivation relaxation pathways, particularly for high  $v$ . Direct measurements for the Treanor pumping (reaction [14]) rate constants are also needed, particularly for  $HF(v > 1) + HF(v > 1)$ , for which no data currently exists. Clarification of these issues would undoubtedly significantly enhance our understanding of the HF laser.

### 4. ACKNOWLEDGMENTS

GCM wishes to acknowledge the National Research Council for support. The authors are grateful for productive discussions with S. R. Leone, F. F. Crim, M. C. Heaven, M. H. Alexander, M. A. Kwok, D. Lyman, and D. W. Setser, as well as helpful comments from the reviewers.



**Table 1: HF Fundamental and Overtone Einstein Emission Coefficients**

Transition	Herbelin & Emanuel <sup>2</sup>	Sileo & Cool <sup>118</sup>	Arunan, Setser & Ogilvie <sup>3</sup>	Zemke et. al. <sup>4</sup>
<b><math>\Delta v = -1</math></b>				
1-0	188.6	189	194.5	203.5
2-1	319.8	324	333.9	348.4
3-2	398.3	410	422.8	439.9
4-3	429.7	453	467.7	484.1
5-4	421.3	460	477.2	487.2
6-5	381.1	436	459.8	455.9
7-6	318.6	386	425.4	397.7
8-7	243.7	317	354.6	320.9
9-8	166.9	236	269.8	235.2
<b><math>\Delta v = -2</math></b>				
2-0	23.4	23.6	23.5	24.7
3-1	67.9	66.2	65.9	70.7
4-2	130.5	124	123.5	134.2
5-3	207.0	193	191.2	212.3
6-4	291.9	271	262.3	301.9
7-5	378.3	354	328.0	399.9
8-6	457.8	443	429.1	501.3
9-7	520.9	536	531.9	599.8
<b><math>\Delta v = -3</math></b>				
3-0	1.2	1.6	1.5	1.6
4-1	4.8	6.1	5.5	5.9
5-2	12.2	14.4	13.1	13.9
6-3	25.0	27.0	25.4	26.1
7-4	44.5	43.9	44.9	43.3
8-5	72.4	64.8	---	66.5
9-6	109.5	89.1	---	96.7

**Table 2: Experimentally determined nascent vibrational distributions for H + F<sub>2</sub>**

v	CFD Kinetics Packages		Experimental Measurements <sup>a</sup>					Recommended <sup>d</sup>
	Cohen & Bott <sup>9</sup> (1977)	Cohen & Bott <sup>10</sup> (1982)	Jonathan et. al. <sup>15</sup> (1972) <sup>b</sup>	Polanyi et. al. <sup>14</sup> (1976) <sup>b</sup>	Tardy et. al. <sup>16</sup> (1988) <sup>c</sup>	Setser et. al. <sup>19</sup> (1979)	Kaufman et. al. <sup>20</sup> (1982)	
0	0.00	0.00	<0.04 (<0.03)	≤0.10 (≤0.08)	0.00 (0.00)	0.00	0.00	0.04 ± 0.04
1	0.00	0.00	0.09 (0.06)	0.12 (0.07)	0.15 (0.14)	0.07	0.06	0.08 ± 0.03
2	0.00	0.00	0.11 (0.08)	0.13 (0.10)	0.13 (0.12)	0.17	0.12	0.13 ± 0.03
3	0.18	0.21	0.13 (0.10)	0.25 (0.20)	0.27 (0.26)	0.28	0.17	0.20 ± 0.07
4	0.30	0.39	0.45 (0.36)	0.35 (0.30)	0.41 (0.40)	0.59	0.37	0.40 ± 0.11
5	0.80	0.70	0.89 (0.83)	0.78 (0.70)	0.72 (0.70)	0.93	0.76	0.78 ± 0.10
6	1.00	1.00	1.00 (1.00)	1.00 (1.00)	1.00 (1.00)	1.00	1.00	1.00
7	0.00	0.45	0.45 (0.43)	0.40 (0.48)	0.76 (0.80)	0.52	0.62	0.50 ± 0.25
8	0.00	0.36	0.20 (0.19)	0.26 (0.37)	0.46 (0.49)	0.00	0.00	0.30 ± 0.15
9	0.00	0.00	<0.04 (<0.01)	0.16 (0.12)	0.41 (0.43)	0.00	0.00	0.15 ± 0.15
10	0.00	0.00	<0.04 (<0.01)	0.00 (0.00)	0.00 (0.00)	0.00	0.00	0.01 ± 0.01

<sup>a</sup> The values in parentheses for Jonathan, Polanyi and Tardy are corrected for the Einstein coefficients of Setser<sup>3</sup>.

<sup>b</sup> The corrected values shown were calculated from the distributions reported by Kaufman<sup>20</sup> which were corrected for the Einstein coefficients of Sileo & Cool<sup>118</sup>.

<sup>c</sup> Tardy<sup>16</sup> originally used the Einstein coefficients of Meredith and Smith<sup>17</sup>.

<sup>d</sup> See text for details

**Table 3: HF total self relaxation rate constants**

Reference	$k_{300}(\text{HF}(v) + \text{HF}) \rightarrow \text{products}, (10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1})$						
	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$	$v = 7$
<b>Experiments</b>							
Bott & Cohen <sup>71</sup>	1.8 ± 0.3						
Hinchen & Hobbs <sup>69</sup>	1.8 ± 0.2						
Bina & Jones <sup>70</sup>	2.3 ± 0.3	5 ± 2					
Kwok & Wilkins <sup>72</sup>	1.6 ± 0.6	16 ± 5	26 ± 9	27 ± 10	(58) <sup>a</sup>	(101) <sup>a</sup>	
Osgood, et. al. <sup>76</sup>	1.7	25 ± 7	49 ± 15	43 ± 18			
Airey & Smith <sup>73</sup>		16	17	≥ 44	≥ 65		
Poole & Smith <sup>74, 75</sup>		13	19	32	46	52	~43
Douglas & Moore <sup>77</sup>			28 ± 4	72 ± 5			
Lampert et. al. <sup>78</sup>			32 ± 6	88 ± 11			
Kaufman <sup>20, 63-66</sup>	1.8	19	31	73	140	290	450
Copeland, et. al. <sup>58</sup>	1.46 ± 0.1	19.8 ± 1.0					
Jursich & Crim <sup>62</sup>			30.2 ± 3.0	72.8 ± 2.7	151 ± 8		
<b>Calculations</b>							
Wilkins & Kwok <sup>79, 80</sup>	1.7	22	29	33	42	51	
Coltrin & Marcus <sup>81, 82</sup>	0.2 ± 0.1	19 ± 3	28 ± 4	53 ± 10	69 ± 10	156 ± 11	455 ± 49
Billing & Poulsen <sup>83</sup>	0.81	6.2 ± 2.2	10 ± 4	19 ± 7	27 ± 10	43 ± 15	82 ± 29
<b>Standard Kinetics Packages<sup>b</sup></b>							
Cohen & Bott 1977 <sup>9</sup>	1.66	6.62	9.94	4.97	16.6	23.2	82.8
Cohen & Bott 1982 <sup>10</sup>	1.66	10.0	28.8	60.9	108.8	174.7	260.9

<sup>a</sup> M. A. Kwok and N. Cohen, personal communication reported in <sup>65</sup>.

<sup>b</sup> only single quantum deactivation rate constants are listed.

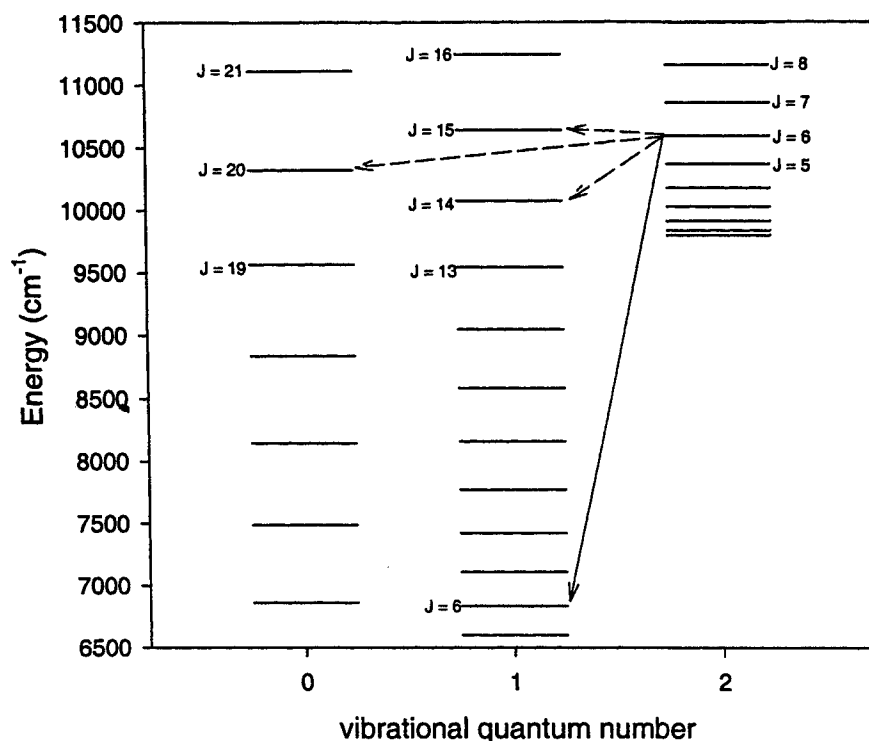
**Table 4: Room Temperature Quenching Rate Constants for HF + H<sub>2</sub>**

Reference	$k_{300}(\text{HF}(v) + \text{H}_2 \rightarrow \text{HF}(v-1) + \text{H}_2) (10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1})$						
	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$	$v = 7$
Bott & Cohen <sup>71, 84</sup>	0.52 ± 0.03						
Poole & Smith <sup>75</sup>		0.21	0.15	0.21	0.49	0.99	1.6
Douglas and Moore <sup>86</sup>			0.31 ± .06	0.47 ± .12			
Bott & Heidner <sup>85</sup>	0.52 ± 0.05		0.35 ± .04				
Kaufman <sup>20</sup>					1.7 ± 0.5	3.5 ± 1	9.1 ± 2.7
Jursich, et. al. <sup>87</sup>			0.38 ± 0.25	0.67 ± 0.10	1.64 ± 0.19		
Cohen & Bott <sup>10</sup>	0.01	0.07	0.21	0.45	0.83	1.35	
<b>Recommended</b>	0.52 ± 0.04	0.20 ± 0.04	0.35 ± 0.04	0.50 ± 0.2	1.6 ± 0.3	3.5 ± 1	9.1 ± 2.7

Table 5: Recommended Rate Constants for the HF laser system

Reaction	Equation	Recommended Rate Constant Expression	References
$F + H_2 \rightarrow HF + H$	$T = 190 - 376 \text{ K:}$ $g(v) * 1.1 \times 10^{-10} e^{-(450 \pm 50)/T}$ $T > 376 \text{ K:}$ $g(v) * 2.2 \pm 0.4 \times 10^{-10} e^{-(595 \pm 50)/T}$	$g(0) = 0.00, g(1) = 0.15$ $g(2) = 0.55, g(3) = 0.30$	10, 39, 43
$H + F_2 \rightarrow HF + F$	$g(v) * 5.0 \times 10^{-15} T^{1.5} e^{-845/T}$	$g(0) = 0.01, g(1) = 0.02, g(2) = 0.04, g(3) = 0.06,$ $g(4) = 0.11, g(5) = 0.22, g(6) = 0.28, g(7) = 0.14,$ $g(8) = 0.08, g(9) = 0.04$	10, 14-16, 19, 20
$H + HF(v) \rightarrow H_2(v') + F$	$v = 3$ $3.0 \times 10^{-11} T^{0.179} e^{-382/T}$ $v = 4 - 6$ $g(v, v') * 1.0 \times 10^{-10} e^{-252/T}$	$g(4,0) = g(4,1) = 0.5, g(5,0) = 0.5, g(5,1) = 1.0,$ $g(6,0) = g(6,1) = 0.5,$ $g(6,2) = 1.5$	10, 53-55
$HF(v) + H_2 \rightarrow HF(v') + H_2$	$g(v) * 1.0 \times 10^{-12}$	$g(1) = 0.52, g(2) = 0.2, g(3) = 0.35, g(4) = 0.50,$ $g(5) = 1.60, g(6) = 3.5, g(7) = 9.1$	10, 20, 71, 84-87
$HF(v) + H_2(v') \rightarrow HF(v-1) + H_2(1)$	$5.2 \pm 0.4 \times 10^{-13}$ $A(v) * 1.7 \times 10^{-8} T^{-1}$ $[\Delta v = -1 \text{ only}]$ $B(v) * 1.7 \times 10^{-12} e^{-352/T}$ $[\Delta v \geq 1]$	$v = 1 \text{ only}$	10, 20, 71, 84-87
$HF(v) + H \rightarrow HF(v') + H$	$g(v) * 2.7 \times 10^{-11} e^{-1359/T}$	$A(3) = 1.4, A(4) = 2.0, A(5) = 2.7, A(6) = 3.5$ $B(1) = 0.4, B(2 - 6) = 0.7$	10, 53, 54
$HF(v) + F \rightarrow HF(v-1) + F$	$A(M) * 1.7 \times 10^{-29} * v * T^{4.5}$	$g(v) = v$ $A(Ar) = 2.0$ $A(F_2) = 2.0$ $A(He) = 3.7$	10, 122
$HF(v) + HF \rightarrow HF(v') + HF$	$v = 1 - 5:$ $k_c * A(v) T^{-1.3}$ $v = 6^a, 300 \text{ K:}$ $2.9 \times 10^{-10}$ $v = 7^a, 300 \text{ K:}$ $4.5 \times 10^{-10}$	$k_c = \pi d^2 \sqrt{\frac{8RT}{\pi \mu}}$ $d = 0.25 \text{ nm}$ $A(1) = 12.0, A(2) = 218.0, A(3) = 315.2,$ $A(4) = 764.0, A(5) = 1610.3$	59, 61, 63
$HF(v) + HF(v') \rightarrow HF(v+1) + HF(v'-1)$	$(v+1)^{0.35} 4.5 \times 10^{-9} T^{-1}$		10, 12
$F + F + M \rightarrow F_2 + M$	$M \times 10^{-34}$	$M(He) = 6 \pm 1$ $M(F_2) = 4.7 \pm 1.2$ $M(Ar) \sim 3$	123, 124

<sup>a</sup> the temperature dependence of  $HF(6-7) + HF$  has not been measured. If the  $T^{-1.3}$  dependence and the expression used for  $v = 1 - 5$  holds, then  $A(6) = 3107$  and  $A(7) = 4339$ .



**Figure 1: Detailed V-T,R relaxation pathways.** The distinction between "true" V-T,R energy transfer and V-R redistribution is shown by the solid and broken lines, respectively. Numerous combinations of HF(1, J) and HF(0, J) states can be populated by HF V-T,R energy transfer. Because of the presence of near-resonant energy levels in  $v = 1$  and 0, V-R redistribution can populate high rotational states of  $v = 0$  and 1. For example, the near resonant V-R redistribution pathways shown in the figure have energy defects of -46.9, 519.6, and 273.7  $\text{cm}^{-1}$ , for relaxation to (1,15), (1,14) and (0,20), respectively. On the other hand, if HF(2, 6) is relaxed to HF(1, 6) by HF(0, J), up to 8 quanta of rotational energy can be transferred to the HF( $v = 0$ ) molecule.

## 5. REFERENCES

1. G. Emanuel, "Numerical Modeling of Chemical Lasers", John Wiley & Sons, New York, 1976.
2. J. M. Herbelin and G. Emanuel, "Einstein coefficients for diatomic molecules", *J. Chem. Phys.*, **60**, 689 - 696, 1974.
3. E. Arunan, D. W. Setser and J. F. Ogilvie, "Vibration-rotational Einstein coefficients for HF/DF and HCl/DCI", *J. Chem. Phys.*, **97**, 1734 - 1741, 1992.
4. W. T. Zemke, W. C. Stwalley, S. R. Langhoff, G. L. Valderrama and M. J. Berry, "Radiative transition probabilities for all vibrational levels in the X1S+ state of HF", *J. Chem. Phys.*, **95**, 7846 - 7853, 1991.
5. J. A. Coxon and P. G. Hajigeorgiou, "Isotopic dependence of Born-Oppenheimer breakdown effects in diatomic hydrides: The B1S+ and X1S+ states of HF and DF", *J. Mol. Spectrosc.*, **142**, 254 - 278, 1990.
6. W. T. Zemke, W. C. Stwalley, J. A. Coxon and P. G. Hajigeorgiou, "Improved potential energy curves and dissociation energies for HF, DF, and TF", *Chem. Phys. Lett.*, **177**, 412 - 418, 1991.
7. J. F. Ogilvie, "The electric dipole moment function of HF", *J. Phys. B*, **21**, 1663 - 1674, 1988.
8. N. Cohen and J. F. Bott, "A Review of Rate Coefficients in the H<sub>2</sub>-F<sub>2</sub> Chemical Laser System", SAMSO-TR-76-82, 1976.
9. N. Cohen, "A Review of Rate Coefficients in the H<sub>2</sub>-F<sub>2</sub> Chemical Laser System - Supplement (1977)", SAMSO-TR-78-41, 1978.
10. N. Cohen and J. F. Bott, "Review of Rate Data for Reactions of Interest in HF and DF Lasers", SD-TR-82-86, 1982.
11. N. Cohen and K. R. Westberg, "Chemical Kinetic Data Sheets for High Temperature Chemical Reactions", *J. Phys. Chem. Ref. Data*, **12**, 531-590, 1983.
12. S. R. Leone, "Rate coefficients for vibrational energy transfer involving the hydrogen halides", *J. Phys. Chem. Ref. Data*, **11**, 953 - 996, 1982.

13. G. A. Hart Jr., "DF Pulsed Chemical Laser Rotational Nonequilibrium Computer Model (PULSDF) and Data Base", NRL Memorandum Report 5051, 1983.
14. J. C. Polanyi and J. J. Sloan, "Energy distribution among reaction products. VII.  $H + F_2$ ", *J. Chem. Phys.*, **57**, 4988 - 4998, 1972.
15. N. Jonathan, S. Okuda and D. Timlin, "Initial vibrational energy distributions determined by infra-red chemiluminescence", *Mol. Phys.*, **24**, 1143 - 1164, 1972.
16. D. C. Tardy and L. L. Feezel, "Chemiluminescence mapping: Pressure-pulse results for  $H(D) + F_2 \rightarrow HF(DF) + F$ ", *Chem. Phys.*, **119**, 89 - 93, 1988.
17. R. E. Meredith and F. G. Smith, "Computation of Electric Dipole Matrix Elements for Hydrogen Fluoride", *J. Quant. Spectrosc. Radiat. Transfer*, **13**, 89-114, 1973.
18. J. K. Cashion, *J. Chem. Phys.*, **39**, 1872, 1963.
19. J. P. Sung, R. J. Malins and D. W. Setser, "Comparison of rate constants for reactions of hydrogen atoms with chlorine, fluorine, iodine chloride, and chlorine fluoride", *J. Phys. Chem.*, **83**, 1007 - 1013, 1979.
20. L. S. Dzelzkalns and F. Kaufman, "Vibrational relaxation of highly excited diatomics. III.  $HF(v = 5, 6, 7) + H_2$ ,  $D_2$ ,  $N_2$ ,  $HF$ ,  $CO_2$ ,  $N_2O$ ,  $CH_4$ , and  $C_2H_6$ ", *J. Chem. Phys.*, **77**, 3508 - 3515, 1982.
21. X. Gimenez, J. M. Lucas, A. Aguilar and A. Lagana, "Calculated versus measured vibrational state specific reactivity of  $H + F_2$ ", *J. Phys. Chem.*, **97**, 1993.
22. S. Bittenson, D. C. Tardy and J. Wana, "Chemiluminescence mapping. I. Experimental method and initial measurements on the  $D + F_2$  and  $F + D_2$  reactions", *Chem. Phys.*, **58**, 313-323, 1981.
23. K. H. Homann, H. Schweinfurth and J. Warnatz, "Rate measurements for the reaction of H atoms with  $F_2$ ", *Ber. Bunsenges. Phys. Chem.*, **81**, 724 - 728, 1977.
24. N. Cohen, note that Refs 10 and 12 list numerous references to "Westberg and Cohen, Int. J. Chem. Kinet. (to be published)." According to a private communication with N. Cohen (The Aerospace Corp., retired) these transition state theory calculations were, in fact, never published.
25. D. L. Baulch, J. Duxbury, S. J. Grant and D. C. Montague, "Homogeneous gas phase reactions of halogen- and cyanide- containing species", *J. Phys. Chem. Ref. Data*, **10**, 1981.
26. S. W. Rabideau, H. G. Hecht and W. B. Lewis, "A study of the kinetics of the reaction between  $H_2$  and  $F_2$  by EPR methods", *J. Magn. Resonance*, **6**, 384, 1972.
27. G. K. Vasil'ev, E. F. Makarov and Y. A. Chernyshev, "Measurement of the chain propagation and termination rate constants for the reaction  $F_2 + H_2(D_2)$  inhibited by  $O_2$ ", *Kinetics and Catalysis*, **16**, 272 - 275, 1975.
28. I. B. Goldberg and G. R. Schneider, "Kinetic study of the reaction of H with  $H_2$  and  $CF_3H$  by ESR methods", *J. Chem. Phys.*, **65**, 147 - 153, 1976.
29. J. Han, M. C. Heaven and G. C. Manke II, "Hydrogen Atom Reactions with Molecular Halogens: The Rate Constants for  $H + F_2$  and  $H + Cl_2$  at 298K", *J. Phys. Chem. A*, **submitted**, 2002.
30. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer and Y. T. Lee, "Molecular beam studies of the  $F + D_2$  and  $F + HD$  reactions", *J. Chem. Phys.*, **82**, 3067 - 3077, 1985.
31. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden and Y. T. Lee, "Molecular beam studies of the  $F + H_2$  reaction", *J. Chem. Phys.*, **82**, 3045 - 3066, 1985.
32. F. Dong, S. H. Lee and K. Liu, "Reactive excitation functions for  $F + p\text{-}H_2/n\text{-}H_2/D_2$  and the vibrational branching for  $F + HD$ ", *J. Chem. Phys.*, **113**, 3633 - 3640, 2000.
33. W. B. Chapman, B. W. Blackmon and D. J. Nesbitt, "State-to-state reactive scattering of  $F + H_2$  in supersonic jets: Nascent rovibrational  $HF(v,J)$  distribution via direct IR laser absorption", *J. Chem. Phys.*, **107**, 8193 - 8196, 1997.
34. S. A. Nizkorodov, W. W. Harper, W. B. Chapman, B. W. Blackmon and D. J. Nesbitt, "Energy-dependent cross sections and nonadiabatic reaction dynamics in  $F(2P_{3/2}, 2P_{1/2}) + n\text{-}H_2 \rightarrow HF(v,J) + H$ ", *J. Chem. Phys.*, **111**, 8404 - 8416, 1999.
35. M. Faubel, L. Y. Rusin, S. Schlemmer, F. Sundermann, U. Tappe and J. P. Toennies, *J. Chem. Soc. Faraday Trans.*, **89**, 1475, 1993.
36. M. Faubel, L. Y. Rusin, S. Schlemmer, F. Sundermann, U. Tappe and J. P. Toennies, *J. Chem. Phys.*, **101**, 2106, 1994.
37. F. J. Aoiz, L. Banares, B. Martinez-Haya, J. F. Castillo, D. E. Manolopoulos, K. Stark and H. J. Werner, "Ab initio simulation of molecular beam experiments for the  $F + H_2 \rightarrow HF + H$  reaction", *J. Phys. Chem. A*, **101**, 6403 - 6414, 1997.
38. V. M. Azriel, G. D. Billing, L. Yu. Rusin and M. B. Sevryuk, "A test of the semiclassical Wigner method for the reaction  $F + H_2 \rightarrow H + HF$ ", *Chem. Phys.*, **195**, 243 - 258, 1995.

39. A. Persky and H. Kornweitz, "The kinetics of the Reaction  $F + H_2 \rightarrow HF + H$ . A critical review of literature data", *Int. J. Chem. Kinet.*, **29**, 67 - 71, 1997.
40. R. Atkinson, D. L. Baulch, R. A. Cox, Jr. R. F. Hampson, J. A. Kerr, M. J. Rossi and J. Troe, *J. Phys. Chem. Ref. Data*, **21**, 1125, 1992.
41. R. Atkinson, D. L. Baulch, R. A. Cox, Jr. R. F. Hampson, J. A. Kerr, M. J. Rossi and J. Troe, *J. Phys. Chem. Ref. Data*, **26**, 521, 1997.
42. R. Atkinson, D. L. Baulch, R. A. Cox, Jr. R. F. Hampson, J. A. Kerr, M. J. Rossi and J. Troe, "Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VIII, Halogen species. IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry", *J. Phys. Chem. Ref. Data*, **29**, 167 - 266, 2000.
43. R. F. Heidner III, J. F. Bott, C. E. Gardner and J. E. Melzer, "Absolute rate coefficients for  $F + H_2$  and  $F + D_2$  at  $T = 295 - 765^\circ$ ", *J. Chem. Phys.*, **72**, 4815 - 4820, 1980.
44. M. A. Kwok, private communication, 2000
45. D. L. Thompson, "Monte Carlo classical trajectory calculation of the rates of H- and D- Atom vibrational relaxation of HF and DF", *J. Chem. Phys.*, **57**, 4170 - 4173, 1972.
46. R. L. Wilkins, "Monte Carlo calculations of reaction rates and energy distribution among reaction products. II.  $H + HF(v) \rightarrow H_2(v) + F$  and  $H + HF(v) \rightarrow HF(v') + H^*$ ", *J. Chem. Phys.*, **47**, 3038 - 3046, 1973.
47. M. Baer, "A coplanar quantum mechanical study of the exchange reaction  $HF + H$ ", *J. Chem. Phys.*, **65**, 493 - 495, 1976.
48. G. C. Schatz and A. Kuppermann, "Vibrational deactivation on chemically reactive potential surfaces: An exact quantum study of a low barrier collinear model of  $H + FH$ ,  $D + FD$ ,  $H + FD$ , and  $D + FH$ ", *J. Chem. Phys.*, **72**, 2737 - 2743, 1980.
49. G. C. Schatz, "A quasiclassical trajectory study of final state distributions in collisions of fast H(D) atoms with  $HF(DF)$ ", *J. Chem. Phys.*, **86**, 6738 - 6744, 1987.
50. C. F. Bender, B. J. Garrison and H. F. Schaefer III, "A critical test of semiempirical  $FH_2$  potential energy surfaces: The barrier height for  $H + FH \rightarrow HF + H$ ", *J. Chem. Phys.*, **62**, 1188 - 1190, 1975.
51. P. Botschwina and W. Meyer, "PNO-CEPA calculation of collinear potential energy barriers for thermoneutral exchange reactions", *Chem. Phys.*, **20**, 43 - 52, 1977.
52. W. R. Wadt and N. W. Winter, "Accurate characterization of the transition state geometry for the  $HF + H' \rightarrow H + HF'$  reaction", *J. Chem. Phys.*, **67**, 3068 - 3073, 1977.
53. R. F. Heidner III and J. F. Bott, "Vibrational deactivation of  $HF(v = 1)$  and  $DF(v = 1)$  by H and D atoms", *J. Chem. Phys.*, **63**, 1810 - 1817, 1975.
54. J. F. Bott and R. F. Heidner III, "The vibrational deactivation of  $HF(v = 3)$  and  $HF(v = 2)$  by H atoms", *J. Chem. Phys.*, **66**, 2878 - 2882, 1977.
55. J. F. Bott and R. F. Heidner III, "Kinetic study of  $H + HF(v = 3)$ : Kinetic isotope effect and temperature dependence", *J. Chem. Phys.*, **68**, 1708 - 1714, 1978.
56. M. A. Kwok and R. L. Wilkins, "Flow tube measurements of  $H + HF(v)$  deactivation rates", *J. Chem. Phys.*, **60**, 2189 - 2190, 1974.
57. N. Cohen and J. F. Bott, It should be noted that the text of Ref. 10 contains  $k(HF(3) + H \rightarrow H_2 + F)$  but the table at the end does not. See pp. 40-42 of Ref. 10.
58. R. A. Copeland, D. J. Pearson, J. M. Robinson and F. F. Crim, "Laser double resonance measurements of vibrational energy transfer rates and mechanisms in  $HF(v = 2)$ ", *J. Chem. Phys.*, **77**, 3974 - 3982, 1982.
59. J. M. Robinson, D. J. Pearson, R. A. Copeland and F. F. Crim, "Rates and Pathways of Vibrational Self-Relaxation of  $Hf(V=2)$  between 300-K and 700-K", *J. Chem. Phys.*, **82**, 780-788, 1985.
60. J. M. Robinson, K. J. Rensberger and F. F. Crim, "A Direct Determination of the Role of Vibration-to-Vibration Energy-Transfer in  $Hf(V=3;4)$  Self-Relaxation", *J. Chem. Phys.*, **84**, 220-226, 1986.
61. T. J. Foster and F. F. Crim, "Vibrational relaxation of  $HF(v = 3, 4, 5)$  between 300 and 700 K", *J. Chem. Phys.*, **75**, 3871 - 3875, 1981.
62. G. M. Jursich and F. F. Crim, "Vibrational relaxation of  $HF(v = 3, 4, 5)$ ", *J. Chem. Phys.*, **74**, 4455 - 4464, 1981.
63. L. S. Dzelzkalns and F. Kaufman, "Vibrational relaxation of highly excited diatomics. IV.  $HF(v = 1 - 7) + CO_2$ ,  $N_2O$ , and  $HF$ ", *J. Chem. Phys.*, **79**, 3836 - 3844, 1983.
64. L. S. Dzelzkalns and F. Kaufman, "Vibrational relaxation of highly excited diatomics. V. The V-V channel in  $HF(v) + HF(0)$  collisions", *J. Chem. Phys.*, **79**, 3363 - 3366, 1983.

65. L. S. Dzelzkalns and F. Kaufman, "Vibrational relaxation of highly excited diatomics. VI.  $\text{DF}(9 \leq v \leq 12) + \text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  and  $\text{HF}(v = 5 - 7) + \text{CO}$ ", *J. Chem. Phys.*, **80**, 6114 - 6121, 1984.
66. L. S. Dzelzkalns and F. Kaufman, "Vibrational relaxation of highly excited diatomics. VII.  $\text{DF}(v = 9 - 12)$  and  $\text{HF}(v = 5 - 7) + \text{HF}(v = 0)$ ,  $\text{DF}(v = 0)$  in all combinations", *J. Chem. Phys.*, **81**, 4975 - 4978, 1984.
67. J. F. Bott, "Gas-dynamic corrections applied to laser-induced fluorescence measurements of  $\text{HF}(v = 1)$  and  $\text{DF}(v = 1)$  deactivation", *J. Chem. Phys.*, **61**, 3414 - 3416, 1974.
68. J. J. Hinchin, "Vibrational relaxation of hydrogen and deuterium fluorides", *J. Chem. Phys.*, **59**, 233 - 240, 1973.
69. J. J. Hinchin and R. H. Hobbs, "Rotational relaxation studies of HF using IR double resonance", *J. Chem. Phys.*, **65**, 2732 - 2739, 1976.
70. M. J. Bina and C. R. Iones, "Use of direct overtone excitation in the measurement of the  $\text{HF}(v = 2)$  deactivation rate", *Appl. Phys. Lett.*, **22**, 44 - 45, 1973.
71. J. F. Bott and N. Cohen, "Temperature dependence of V-V and V-R,T energy transfer measurements in mixtures containing  $\text{HF}^*$ ", *J. Chem. Phys.*, **58**, 4539 - 4549, 1973.
72. M. A. Kwok and R. L. Wilkins, "Flow-tube studies of vibrational energy transfer in  $\text{HF}(v) + \text{HF}$ ,  $\text{DF}(v) + \text{HF}$ , and  $\text{DF}(v) + \text{D}_2$  systems", *J. Chem. Phys.*, **63**, 2453 - 2460, 1975.
73. J. R. Airey and I. W. M. Smith, "Quenching of infrared chemiluminescence: Rates of energy transfer from  $\text{HF}(v \leq 5)$  to  $\text{CO}_2$  and  $\text{HF}$ , and from  $\text{DF}(v \leq 3)$  to  $\text{CO}_2$  and  $\text{HF}^*$ ", *J. Chem. Phys.*, **57**, 1669 - 1676, 1972.
74. P. R. Poole and I. W. M. Smith, "Quenching of infrared chemiluminescence. Part 7. Rates of energy transfer from  $\text{HF}(v = 2 - 7)$  and  $\text{DF}(v = 3 - 5)$  to a wide range of collision partners", *J. Chem. Soc. Faraday Trans. 2*, **73**, 1447 - 1458, 1977.
75. P. R. Poole and I. W. M. Smith, "Quenching of infrared chemiluminescence. Part 6. Rates of energy transfer from  $\text{HF}(v = 2 - 7)$  to  $\text{HF}(v = 0)$ ,  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{HD}$ , and from  $\text{DF}(v = 3 - 5)$  to  $\text{HF}(v = 0)$ ", *J. Chem. Soc. Faraday Trans. 2*, **73**, 1434 - 1446, 1977.
76. R. M. Osgood Jr., P. B. Sackett and A. Javan, "Measurement of vibrational-vibrational exchange rates for excited vibrational levels ( $2 \leq v \leq 4$ ) in hydrogen fluoride gas", *J. Chem. Phys.*, **60**, 1464 - 1480, 1974.
77. D. J. Douglas and C. B. Moore, "Vibrational Relaxation of  $\text{HF}(v = 3, 4)$ ", *Chem. Phys. Lett.*, **57**, 485, 1978.
78. J. K. Lampert, G. M. Jursich and F. F. Crim, "Collisional relaxation of  $\text{HF}(v = 3, 4)$  by  $\text{HF}$ ,  $\text{CH}_4$ , and  $\text{CD}_4$ ", *Chem. Phys. Lett.*, **71**, 258 - 263, 1980.
79. R. L. Wilkins, "Mechanisms of energy transfer in hydrogen fluoride systems", *J. Chem. Phys.*, **67**, 5838 - 5854, 1977.
80. R. L. Wilkins and M. A. Kwok, "Temperature dependence of vibrational relaxation from the upper vibrational levels of  $\text{HF}$  and  $\text{DF}$ ", *J. Chem. Phys.*, **73**, 3198 - 3204, 1980.
81. M. E. Coltrin and R. A. Marcus, "Cross-correlation trajectory study of vibrational relaxation of  $\text{DF}(v = 1 - 7)$  by  $\text{DF}(v = 0)$  and of  $\text{HF}$  by  $\text{HF}$ ", *J. Chem. Phys.*, **76**, 2379 - 2383, 1982.
82. M. E. Coltrin and R. A. Marcus, "Cross correlation trajectory study of vibrational relaxation of  $\text{HF}(v = 1 - 7)$  by  $\text{HF}(v = 0)$ ", *J. Chem. Phys.*, **73**, 4390 - 4396, 1980.
83. G. D. Billing and L. L. Poulsen, "Theory of V-V and V-T/R energy transfer for  $\text{HF}(v = 1 - 7) + \text{HF}(0)$ ", *J. Chem. Phys.*, **68**, 5128 - 5138, 1978.
84. J. F. Bott, "Vibrational relaxation of  $\text{HF}(v = 1)$  and  $\text{DF}(v = 1)$  by  $\text{H}_2$  and  $\text{D}_2$ ", *J. Chem. Phys.*, **61**, 2530 - 2535, 1974.
85. J. F. Bott and R. F. Heidner III, "Vibrational relaxation of  $\text{HF}(v = 1 \text{ and } 3)$  in  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{D}_2$  at 200 and 295 K", *J. Chem. Phys.*, **72**, 3211 - 3215, 1980.
86. D. J. Douglas and C. B. Moore, "Vibrational relaxation of  $\text{HF}(v = 3, 4)$  by  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{CO}_2$ ", *J. Chem. Phys.*, **70**, 1769 - 1773, 1979.
87. G. M. Jursich, D. R. Ritter and F. F. Crim, "Vibrational relaxation of  $\text{HF}(v = 3, 4, \text{ and } 5)$  by  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{CH}_4$ ,  $\text{CD}_4$ , and  $\text{CO}_2$ ", *J. Chem. Phys.*, **80**, 4097 - 4104, 1984.
88. N. Cohen, J. F. Bott, M. A. Kwok and R. L. Wilkins, "The status of rotational nonequilibrium in HF chemical lasers", SD-TR-86-26, 1986.
89. M. A. Kwok, R. L. Wilkins, G. I. Segal, E. F. Cross, R. H. Ueunten and K. L. Foster, "In search of high J states in the  $\text{HF}(v, J)$  system", SD-TR-85-21, 1985.
90. E. Cuellar and G. C. Pimentel, "Rotational laser emission by HF in the  $\text{ClF-H}_2$  chemical laser", *J. Chem. Phys.*, **71**, 1385 - 1391, 1979.



91. E. R. Sirkin and G. C. Pimentel, "HF rotational laser emission through photoelimination from vinyl fluoride and 1,1-difluoroethene", *J. Chem. Phys.*, **75**, 604 - 612, 1981.
92. E. R. Sirkin and G. C. Pimentel, "HF rotational lasers: Enhancement of V $\rightarrow$ R multi-quantum energy transfer by CO and CO<sub>2</sub>", *J. Chem. Phys.*, **77**, 1314 - 1322, 1982.
93. G. L. Richmond and G. C. Pimentel, "HF rotational laser emission from ClF/H<sub>2</sub> reaction: Time evolution of the gain", *J. Chem. Phys.*, **80**, 1162 - 1170, 1984.
94. J. H. Smith and D. W. Robinson, "Chemical pumping of pure rotational HF lasers", *J. Chem. Phys.*, **74**, 5111 - 5115, 1981.
95. J. H. Smith and D. W. Robinson, "The OH and OD laser: Collision-induced energy transfer pumping", *J. Chem. Phys.*, **68**, 5474 - 5480, 1978.
96. J. H. Smith and D. W. Robinson, "Pure rotational lasing in four electronic states of NH: Impulsive to adiabatic collisional pumping", *J. Chem. Phys.*, **71**, 271 - 280, 1979.
97. E. Arunan, D. Raybone and D. W. Setser, "Vibrational relaxation rate constants for HF( $v = 1 - 4$ ) by CO, CO<sub>2</sub>, and HCN with product identification by infrared emission", *J. Chem. Phys.*, **97**, 6348 - 6362, 1992.
98. D. Raybone, S. J. Wategaonkar and D. W. Setser, "Near resonant V-R,T energy transfer in the relaxation of vibrationally excited HF by CO", *J. Chem. Phys.*, **89**, 3384 - 3386, 1988.
99. D. L. Thompson, "A Monte Carlo quasiclassical trajectory study of energy transfer in Ar + HF collisions", *J. Chem. Phys.*, **76**, 5947 - 5967, 1982.
100. D. L. Thompson, "Vibrational-rotational energy transfer in collisions of HF( $v = 4$ ,  $J = 20$ ) with rare gases", *J. Chem. Phys.*, **78**, 1763 - 1766, 1983.
101. H. K. Haugen, W. H. Pence and S. R. Leone, "Infrared double resonance spectroscopy of V-T,R relaxation of HF( $v = 1$ ): Direct measurement of high- $J$  populations", *J. Chem. Phys.*, **80**, 1839 - 1852, 1984.
102. M. A. Muyskens, Ph.D. Thesis, University of Wisconsin, Madison, 1989.
103. R. A. Copeland, D. J. Pearson and F. F. Crim, "Laser double resonance measurements of rotational energy transfer rates in HF( $v = 2$ )", *Chem. Phys. Lett.*, **81**, 541 - 546, 1981.
104. R. A. Copeland and F. F. Crim, "Rotational energy transfer in HF( $v = 2$ ): Double resonance measurements and fitting law analysis", *J. Chem. Phys.*, **78**, 5551 - 5563, 1983.
105. R. A. Copeland and F. F. Crim, "Rotational energy transfer in HF( $v = 2$ ): Energy corrected sudden approximation scaling relations applied to double resonance measurements", *J. Chem. Phys.*, **81**, 5819 - 5829, 1984.
106. R. A. Copeland, Ph.D. Thesis, University of Wisconsin, Madison, 1982.
107. C. A. Taatjes and S. R. Leone, "Laser double-resonance measurements of rotational relaxation rates of HF( $J = 13$ ) with rare gases, H<sub>2</sub>, and D<sub>2</sub>", *J. Chem. Phys.*, **89**, 302 - 308, 1988.
108. C. A. Taatjes and S. R. Leone, "Laser double-resonance studies of low-temperature rotational and vibrational relaxation of HF: Rates for HF( $J = 13$ ) + HF from 225 to 298 K and detection of HF( $v = 1$ ) deactivation by HF clusters at 210 - 240 K", *J. Phys. Chem.*, **95**, 5870 - 5877, 1991.
109. L. A. Bollati, G. A. Arguello and E. H. Staricco, "Dependence on vibrational excitation of energy transfer processes for HF( $v, J$ ) + HF( $v = 0$ )", *J. Chem. Phys.*, **83**, 6050 - 6052, 1985.
110. L. A. Bollati, G. A. Arguello and E. H. Staricco, "HF autorelaxation in  $v = 1$  and  $v = 2$ ", *J. Chem. Soc. Faraday Trans. 2*, **84**, 599 - 609, 1988.
111. R. L. Wilkins and M. A. Kwok, "Rotational energy transfer in HF", *J. Chem. Phys.*, **78**, 7153 - 7158, 1983.
112. R. L. Wilkins and M. A. Kwok, "Temperature dependence of HF( $v = 1$ ) + HF( $v = 2$ ) vibrational relaxation", *J. Chem. Phys.*, **70**, 1705 - 1710, 1979.
113. D. L. Thompson, N. C. Blais and D. G. Truhlar, "Rotational energy transfer in collisions of internally excited molecules. Effect of initial conditions and potential energy surface", *J. Chem. Phys.*, **78**, 1335 - 1338, 1983.
114. D. L. Thompson, "Vibrational and rotational energy transfer in Ar + HF", *Chem. Phys. Lett.*, **84**, 397 - 400, 1981.
115. G. D. Billing, "Cross-sections for rotational/vibrational transitions in HF-HF collisions: Effect of initial state", *Chem. Phys.*, **112**, 95 - 104, 1986.
116. G. D. Billing, "Semiclassical calculation of cross sections for vibration-rotation energy transfer in HF-HF collisions", *J. Chem. Phys.*, **84**, 2593 - 2603, 1986.
117. L. L. Poulsen and G. D. Billing, "A classical trajectory study of the fate of vibrational energy released in HF", *Chem. Phys.*, **53**, 389 - 401, 1980.
118. R. N. Sileo and T. A. Cool, "Overtone emission spectroscopy of HF and DF: Vibrational matrix elements and dipole moment function", *J. Chem. Phys.*, **65**, 117 - 133, 1976.

119. G. P. Quigley and G. J. Wolga, "The deactivation of HF( $v = 1$ ) and DF( $v = 1$ ) by O, Cl, and F atoms", *J. Chem. Phys.*, **63**, 5263 - 5268, 1975.
120. J. A. Blauer and W. C. Solomon, "Deactivation of vibrationally excited hydrogen fluoride ( $v = 2$  and  $v = 1$ ) by atomic fluorine", *Int. J. Chem. Kinet.*, **5**, 553 - 558, 1973.
121. J. F. Bott and N. Cohen, "HF vibrational relaxation by F atoms", *J. Chem. Phys.*, **55**, 5124 - 5125, 1971.
122. J. F. Bott, "Vibrational relaxation of DF by He and Ar", *J. Chem. Phys.*, **63**, 2253 - 2254, 1975.
123. A. A. Vasiliev, V. N. Bezmelnitsyn, V. F. Sinianski and B. B. Chaivanov, "Rate constant for heterogeneous dissociation of fluorine in a temperature range of 700 - 900 K on a nickel surface", *J. Fluorine Chem.*, **95**, 153 - 159, 1999.
124. C. J. Ultee, "The homogeneous recombination rate constant of F atoms at room temperature", *Chem. Phys. Lett.*, **46**, 366 - 367, 1977.